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On the discotic nematic-isotropic transition properties effect of quadrupole interaction

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Abstract : A statistical mechanical perturbation theory is applied to analyse the influence of quadrupole interaction on a variety of thermodynamic properties of discotic nematic liquid crystals. Numerical calculations are reported for a model system in which molecules are assumed to interact via a pair potential having both repulsive and attractive parts. The repulsive interaction is represented by a repulsion between hard oblate ellipsoid of revolution and is a short-range, rapidly varying potential. The attractive potential, a function of only the centre of mass distance, and the relative orientation bwteen the two molecules, is represented by the isotropic dispersion and anisotropic quadrupole interaction between two asymmetric molecules. The properties of the reference system and the first order perturbation term are evaluated by assuming that an angle-dependent range parameter scales the pair correlation function such that it decouples the orientational degrees of freedom from the translational one. It is observed that the phase transition properties are highly sensitive to the form of effective one-body orientational potential. The influence of pressure on the stability, ordering and thermodynamic phase transition properties is analysed. We observe a remarkable symmetry in the transition properties between prolate ellipsoids (ordering nematic) and oblate ellipsoids (discotic nematic).

Keywords : Liquid crystals, quadrupole interaction, perturbation theory

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1. Introduction

The liquid crystal molecules possess a strong anisotropy in both intermolecular repulsions and attractions. As a result, in the construction of a molecular theory one faces the complication of dealing with both spatial and angular variables of the molecules [1]. Several attempts have been made to develop theories [1-8] in which both hard core repulsions and angle dependent attractions are explicitly included. This has been done within the lattice model framework by Alben [9], Flory and Ronca [2] and Warner [3]. Dowell [4] has carried out this work still further by including the effect of soft repulsions and multiple-site attractions. While Ypma and Vertogen [5] have used deformed hard sphere model and Bellmann type expansion to calculate the properties of the reference system, Savithramma and Madhusudana [6] used scaled particle theory. All these methods differ only in evaluating the properties of reference system and are identical as far as attractive interaction is concerned.

Recently, another type of molecular theory has been developed by Singh [10] and others [11-13]. These works are based on a density functional approach [14, 15] which allows writing formally exact expressions for thermodynamic functions and one-particle distribution functions in terms of the direct correlation functions. This type of theories are physically more reasonable than those of Maier-Saupe [16] or repulsion dominant type of theories [17]. However, the major difficulty with these theories is associated with the evaluation of this purpose.

In a previous publication Singh *et al* [18] (referred to as I) have used a statistical mechanical perturbation theory, as developed by Singh and Singh [1], to describe the equilibrium properties of discotic nematic liquid crystals. In the present paper the same type of investigation as that of I has been extended to analyse the influence of quadrupole interaction on the thermodynamic and orientational properties of discotic nematic-isotropic phase transition. The role of pressure on the phase transition behaviour has also been studied. In the following section a brief account of the theory and the working equations are summarized. The result and discussion are given in Section 3.

2. Theory and working equations

We consider a system of N axially symmetric discotic nematic molecules contained in a volume V at temperature T. Assuming that the total potential energy of interaction of the system is pairwise additive, we write

$$U_N(x_1, x_2, \ldots, x_N) = \sum_{1 \le i < j \le N} u(x_i, x_j) \tag{1}$$

where the vector x_i $(= r_i, \Omega_i)$ represents both the location r_i of the centre of mass of the i-th molecule and its relative orientation Ω_i described by Euler angles θ_i, ϕ_i and ψ_i. The volume element dx_i is equivalent to $d^3r_i\, d\Omega_i$ where $d^3r_i = dx_i\, dy_i\, dz_i$ and $d\Omega_i = \frac{1}{4\pi} \sin\theta_i\, d\theta_i\, d\phi_i\, d\psi_i$

In developing a perturbation theory we begin by writing the pair potential energy of interaction $u(x_i, x_j)$ as a sum of two parts - one part of this division is known as the reference potential u_o and the other perturbation potential u_p, i.e.

$$u(x_i, x_j) = u_o(x_i, x_j) + \lambda u_p(x_i, x_j) \tag{2}$$

where $u_o(x_i, x_j)$ is chosen to include the rapidly varying short-range repulsive part of the interaction and $u_p(x_i, x_j)$ contains the more smoothly varying long-range attractive part. λ is a perturbation parameter. For $\lambda = 0$, the total potential reduces to the reference potential, whereas for $\lambda = 1$, $u(x_i, x_j)$ becomes the full potential. Thus by increasing the value of λ from 0 to 1, the perturbation is generally switched on. A perturbation calculation generally proceeds in two steps . The first task is to calculate the effect of the perturbation on the thermodynamic properties and pair distribution function of the reference system. The second step is to find a recipe to relate the properties of the reference system to that of a system the properties of which are already known to a high degree of accuracy. A useful theory is one

which converges at the first-order term.

Following the statistical mechanical machinery as outlined by Singh and Singh [1], we write the perturbation series for the Helmholtz free-energy as

$$\frac{\beta A}{N} = \frac{\beta A^{(o)}}{N} + \sum_{t=1}^{\infty} \frac{\beta A^{(t)}}{N} \tag{3}$$

where $A^{(o)}$ is the reference system contribution to A and

$$\frac{\beta A^{(t)}}{N} = \beta \int f(\Omega_1), d\Omega_1 \, \psi^{(t)}(\Omega_1) \tag{4}$$

represents the perturbation terms described by the attractive potential, t denotes the order of perturbation and $\psi^{(t)}(\Omega_1)$ is defined as effective one-body orientational perturbation potential

$$\psi^{(t)}(\Omega_1) = \frac{1}{2t} \rho \int f(\Omega_2)\, d\Omega_2 \int dr_{12}\, u_p(r_{12}, \Omega_1, \Omega_2)\, g^{(t-1)}(r_{12}, \Omega_1, \Omega_2) \tag{5}$$

$f(\Omega)$ is the one-particale orientational distribution function.

The first order perturbation term is written as

$$\frac{\beta A^{(1)}}{N} = \beta \int f(\Omega_1)\, d\Omega_1 \psi^{(1)}(\Omega_1) \tag{6}$$

where

$$\psi^{(1)}(\Omega_1) = \frac{1}{2} \rho \int f(\Omega_2)\, d\Omega_2 \int dr_{12}\, u_p(r_{12}, \Omega_1, \Omega_2)\, g^{(0)}(r_{12}, \Omega_1, \Omega_2) \tag{7}$$

Here $g^{(0)}(r_{12}, \Omega_1, \Omega_2)$ is the pair correlation function for the reference system.

We consider a model system in which the pair potential energy eq. (2) is written as

$$u(r_{12}, \Omega_1, \Omega_2) = u_{hr}(r_{12}, \Omega_1, \Omega_2) + u_p(r_{12}, \Omega_1, \Omega_2) \tag{8}$$

where $u_{hr}(r_{12}, \Omega_1, \Omega_2)$ represents the repulsion between hard ellipsoids of revolution parametrized by the length-to-width ratio x ($=a/b$, $2a$ and $2b$ denote, respectively, the lengths of major and minor axes of the ellipsoids), and satisfies the relation

$$u_{hr}(r_{12}, \Omega_1, \Omega_2) = \begin{cases} \infty, & \text{for } r_{12} \le D(\hat{r}_{12}, \Omega_{12}) \\ 0, & \text{for } r_{12} > D(\hat{r}_{12}, \Omega_{12}) \end{cases} \tag{9}$$

$D(\hat{r}_{12}, \Omega_{12})$ is the distance of closest approach of two molecules with relative orientation Ω_{12}. $\hat{r}_{12} = r_{12} / |r_{12}|$ is a unit vector along the intermolecular axis. We adopt following form for u_p,

$$u_p(r_{12}, \Omega_1, \Omega_2) = u_p(r_{12}, \Omega_{12}) = \begin{cases} -r^{-6} C_t - r^{-5} C_q P_2(\cos\theta_{12}); & \text{for } r_{12} > D(\hat{r}_{12}, \Omega_{12}) \\ 0 & ; \text{for } r_{12} \le D(\hat{r}_{12}, \Omega_{12}) \end{cases} \tag{10}$$

The first term of eq. (10) represents the isotropic component of dispersion interaction and the second term is the anisotropic quadrupole interaction. C_t and C_q are the respective constants. θ_{12} is the angle between the orientation of the two molecules. The potential (10)

depends on the intermolecular separation but not on the orientation of the intermolecular vector. It also depends on the relative angle between the two molecules alone and not on their orientations Ω_1 and Ω_2. This is certainly a drastic over simplification of the intermolecular potential of the real liquid crystals. However, there are two reasons of our choice of such a simple trial potential (8). First, such a pair potential is in accord with the Maier-Saupe theory, and so enables us to test the molecular field approximation employed in the theory when there is a translational disorder. Secondly, it provides a convenient means to study the effects of molecular interactions on the thermodynamic properties of the system.

In order to calculate the thermodynamic properties of a system of hard ellipsoids interacting via a pair potential (9) we start with pressure equation

$$\frac{\beta p_o}{\rho} = 1 - \frac{1}{6}\beta\rho \int dr_{12} \int f(\Omega_1)\, d\Omega_1 \int f(\Omega_2)\, d\Omega_2 \left[r_{12} \nabla u_{hr}(r_{12}, \Omega_{12})\, g^{(0)}(r_{12}, \Omega_{12})\right] \tag{11}$$

The operator ∇ acts on the r_{12} coordinates of $u_{hr}(r_{12}, \Omega_{12})$ only. The expression (11) is difficult to evaluate because very little information is known about the unknown function $g^{(0)}(r_{12}, \Omega_{12})$. We evaluate eq. (11) using decoupling approximation [19] which amount to assume

$$g^{(0)}(r_{12}, \Omega_{12}) \simeq g^{(0)}(r_{12}/D(\hat{r}_{12}, \Omega_{12})) = g^{(0)}(r^*_{12}) \tag{12}$$

This approximation completely decouples the orientational and positional degrees of freedom. The error introduced in using eq. (12) at liquid density is difficult to assess but it is similar to a mean-field approximation for the orientational part of the interaction.

Taking Berne and Pechukas [20] relation for $D(\hat{r}_{12}, \Omega_{12})$;

$$D(\hat{r}_{12}, \Omega_{12}) = d_o \left[1 - \frac{\chi}{2}\left\{\frac{(\hat{r}_{12}.\hat{e}_1 + \hat{r}_{12}\hat{e}_2)^2}{1 + \chi(\hat{e}_1.\hat{e}_2)} + \frac{(\hat{r}_{12}.\hat{e}_1 - \hat{r}_{12}.\hat{e}_2)^2}{1 - \chi(\hat{e}_1.\hat{e}_2)}\right\}\right]^{-1/2} \tag{13}$$

and reducing the distance variable with $D(\hat{r}_{12}, \Omega_{12})$ and using eq. (12), we get

$$\frac{\beta p_o}{\rho} = 1 + \frac{2\eta(2-\eta)}{(1-\eta)^3}\left(F_0(\chi) - F_2(\chi)\bar{P}_2^2 - F_4(\chi)\bar{P}_4^2\right) \tag{14}$$

where

$$\eta = \rho v_o \tag{14a}$$

$$F_0(\chi) = (1-\chi^2)^{1/2}\left(1 - \frac{1}{6}\chi^2 - \frac{1}{40}\chi^4 - \frac{1}{112}\chi^6 - \ldots\right) \tag{14b}$$

$$F_2(\chi) = \frac{1}{3}\chi^2(1-\chi^2)^{1/2}\left(1 + \frac{3}{14}\chi^2 + \frac{5}{56}\chi^4 + \frac{25}{528}\chi^6 + \ldots\right) \tag{14c}$$

$$F_4(\chi) = \frac{1}{35}\chi^4(1-\chi^2)^{1/2}\left(1 + \frac{15}{22}\chi^2 + \frac{525}{1184}\chi^4 + \ldots\right) \tag{14d}$$

$$\bar{P}_n = \int d\Omega f(\Omega) P_n(\cos\theta) \tag{14e}$$

$$\chi = \frac{x^2 - 1}{x^2 + 1} \tag{14f}$$

v_o is the volume of a molecule, $d_o = 2a$, $\hat{e}_1$ and $\hat{e}_2$ are unit vectors along the symmetry axis of two interacting molecules.

The Helmholtz free-energy per particle for the reference system can now be evaluated using standard thermodynamic relation and we get

$$\frac{\beta A^{(0)}}{N} = (\ln\rho - 1) + < \ln [4\pi f(\Omega)] > + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \left(F_o(\chi) - F_2(\chi)\, \bar{P}_2^{\,2} - F_4(\chi)\, \bar{P}_4^{\,2}\right) \tag{15}$$

where the first two terms represent the free-energy of a gas of noninteracting particles and the last term arises due to the interparticle interaction.

Using eqs. (10), (12) and reducing the distance variables with $D(\hat{r}_{12}, \Omega_{12})$, the Helmholtz free-energy in the first order perturbation is written as

$$\frac{\beta A^{(1)}}{N} = \frac{1}{2} \beta\rho \int f(\Omega_1)\, d\Omega_1 \int f(\Omega_2)\, d\Omega_2\, Y(\Omega_{12}) \tag{16}$$

where

$$Y(\Omega_{12}) = - C_t I_6 (\rho, T)\, I_6 (\theta_{12}) - C_q I_5 (\rho, T)\, I_5 (\theta_{12})\, P_2 (\cos \theta_{12}) \tag{17}$$

with

$$I_n (\rho, T) = \int_0^\infty dr^*_{12}\, r^{*2}_{12}\, {}^n g_{hs}^{(0)} (r^*_{12}) \tag{18}$$

$$I_n (\theta_{12}) = \int d\hat{r}_{12}\, D^3\, {}^n (\hat{r}_{12}, \Omega_{12}) \tag{19}$$

Using eq. (13) we evaluate the integral (19) for n= 5 and 6 for fixed orientations $\hat{e}_1.\hat{e}_2$ = cos θ_{12}. For convenience we write our result as an expansion in the Legendre functions

$$I_n (\theta_{12}) = d_o^{\,3-n} [A_o^{(n)} + A_2^{(n)} P_2(\cos \theta_{12}) + A_4^{(n)} P_4 (\cos \theta_{12}) + \ldots] \tag{20}$$

The values of the constants $A_m^{(n)}$ are determined as a function of length-width ratio x. The values for m = 0, 2 and 4 and n = 5 and 6 are tabulated in *I* for x = 0.6, 0.7, 0.8 and 0.9.

Using the exact radial distribution function for hard spheres obtained from computer simulation the integral (18) can be evaluated. Combining the known density expansion for $g_{hs}^{(0)} (r^*_{12})$ with the Monte-Carlo values, Larsen *et al* [21] have proposed the following extended series

$$I_n (\rho^*) = J_{o,n} + J_{1,n} \rho^* + J_{2,n} \rho^{*2} + J_{3,n} \rho^{*3} + J_{4,n} \rho^{*4} + J_{5,n} \rho^{*5} \tag{21}$$

where $\rho^* = \frac{6}{\pi} \rho v_o$. The coefficients $J_{m,n}$'s are tabulated by Larsen *et al* [21] for several values of n (= 0 to 24).

Substituting eqs. (20) and (21) into eq. (17) we get

$$\frac{\beta A^{(1)}}{N} = \beta (- \phi_o - \phi_2 \bar{P}_2^{\,2} - \phi_4 \bar{P}_4^{\,2}) \tag{22}$$

where

$$\phi_0 = \left(\frac{\pi\alpha}{12}\right) C^*_{\iota} A_0^{(6)} \eta I_6(\eta) + \frac{1}{10}\left(\frac{\pi\alpha}{6}\right)^{2/3} C^*_q A_2^{(5)} \eta I_5(\eta) \tag{22a}$$

$$\phi_2 = \left(\frac{\pi\alpha}{12}\right) C^*_{\iota} A_2^{(6)} \eta I_6(\eta) + \frac{1}{2}\left(\frac{\pi\alpha}{6}\right)^{2/3} C^*_q \left[A_0^{(5)} + \frac{2}{7}(A_2^{(5)} + A_4^{(5)})\right] \eta I_5(\eta) \tag{22b}$$

and

$$\phi_4 = \left(\frac{\pi\alpha}{12}\right) C^*_{\iota} A_4^{(6)} \eta I_6(\eta) + \frac{1}{2}\left(\frac{\pi\alpha}{6}\right)^{2/3} C^*_q \left[\frac{18}{35} A_2^{(5)} + \frac{20}{77} A_4^{(5)}\right] \eta I_5(\eta) \tag{22c}$$

Here $C^*_{\iota} = C_{\iota}/v_0^2$ and $C^*_q = C_q / v_0^{5/3}$

With the help of relations (15) and (22) the total configurational Helmholtz free-energy can be written as

$$\frac{\beta A}{N} = \langle \ln [4\pi f(\Omega)] \rangle + B_0(\eta, T) - B_2(\eta, T) \bar{P}_2^2 - B_4(\eta, T) \bar{P}_4^2 \tag{23}$$

where

$$B_0(\eta, T) = \ln \rho - 1 + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_0(\chi) - \beta\phi_0 \tag{23a}$$

$$B_2(\eta, T) = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_2(\chi) + \beta\phi_2 \tag{23b}$$

$$B_4(\eta, T) = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} F_4(\chi) + \beta\phi_4 \tag{23c}$$

The minimization of free-energy with respect to the variation of $f(\Omega)$ subject to the constraint

$$\int f(\Omega)\, d\Omega = 1 \tag{24}$$

determines one-particle orientational distribution at a fixed temperature and pressure. The form of $f(\Omega)$ is obtained from the eqs. (23) and (24),

$$f(\Omega) = \frac{\exp [2B_2 \bar{P}_2 P_2(\cos\theta) + 2B_4 \bar{P}_4 P_4(\cos\theta)]}{\int \exp [2B_2 \bar{P}_2 P_2(\cos\theta) + 2B_4 \bar{P}_4 P_4(\cos\theta)]\, d\Omega} \tag{25}$$

which leads directly to the trancedental equations for the second and fourth rank order parameters defined by

$$\bar{P}_2 = \int f(\Omega)\, d\Omega\, P_2(\cos\theta) \tag{26}$$

$$\bar{P}_4 = \int f(\Omega)\, d\Omega\, P_4(\cos\theta) \tag{27}$$

The nematic-isotropic transition at constant pressure is located by equating the pressures and chemical potentials of the two phases,

$$P_{\text{nem.}}(\eta, T_{NI}, \bar{P}_{2NI}, \bar{P}_{4NI}) = P_{\text{iso}}(\eta_i, T_{NI}) \tag{28}$$

$$\mu_{\text{nem.}}(\eta, T_{NI}, \bar{P}_{2NI}, \bar{P}_{4NI}) = \mu_{\text{iso}}(\eta_i, T_{NI}) \tag{29}$$

$\bar{P}_{2NI}$ and $\bar{P}_{4NI}$ are determined from eqs. (26) and (27). Keeping the pressure fixed, we get five equations involving five unknowns η, η_i, T_{NI}, $\bar{P}_{2NI}$ and $\bar{P}_{4NI}$. In principles, these parameters can be determined by solving simultaneously eqs. (26)-(29).

But, in practice, these equations are too complex to be solved analytically. We solve them numerically by an iterative procedure.

Other thermodynamic properties such as pressure, chemical potential, etc., can be derived from eqs. (15) and (22) using standard thermodynamic relations.

3. Results and discussions

We investigate first the effects of length-to-width ratio and potential parameters C_t and C_q as defined in eq. (10) on the thermodynamic properties of nematic-isotropic phase transition of ordinary nematic (rod shape) as well as discotic nematic phases. We perform the calculation in a way as described in I. For ordinary nematic phase similar investigation as that of I has been carried out by Singh and Singh [7]. The present work includes both $\bar{P}_2$ and $\bar{P}_4$ terms in eq. (23) whereas in I and [7] only the $\bar{P}_2$ term is included. For a given x at the atmospheric pressure $p = 1$ bar the potential parameters C_1 and C_t/C_q are selected so as to reproduce quantitatively the transition temperature $T_{NI} \simeq 409$ K (for the ordinary nematic phase) and $\simeq 600$ K (for the discotic nematic phase). These values correspond, respectively, to the T_{NI} of PAA (ordinary nematic) and hexa-η-hexyloxy benzoate of triphenylene (discotic phase). Other transition parameters are determined self-consistently by an iterative procedure.

The discotic nematic-isotropic (DNI) transition parameters are determined at constant values of pressure ranging from 1 bar to 500 bar. The results obtained are summarized in Tables 1 and 2. The parameter Γ listed in the tables measures the relative sensitivity of the order parameter to volume change (at constant temperature) and the temperature change (at constant volume),

$$\Gamma = \frac{V}{T}\left(\frac{(\partial \bar{P}_2 / \partial V)_T}{(\partial \bar{P}_2 / \partial T)_V}\right) = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_{\bar{P}_2} = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_{\bar{P}_2},$$

The pressure dependence of the transition temperature (dT_{NI}/dp) is determined by Clausius-Clapeyron's law. $\Delta S/NK$ measures the entropy change at the transition. From these numerical results it can be seen that in both the cases in I ($\bar{P}_4$ term not included in eq. (23)) as well as in the present work the relative density change at the transition $\Delta\eta/\eta$ decreases as the ratio C_t/C_q increases (i.e. the relative strength of quadrupole interaction decreases) for a given value of C^*_t. A slow increase in the value of packing fraction η is observed with increasing C_t/C_q. Comparing the results obtained here with the corresponding results obtained in I, we observe an increase in the value of the packing fraction η, relative density change $\Delta\eta/\eta$, second order Legendre polynomial order parameter $\bar{P}_{2NI}$, transition entropy and dT_{NI}/dp due to the inclusion of fourth Legendre polynomial order parameter $\bar{P}_{4NI}$. From the tables it is also observed that for a given x and interaction parameters, as pressure increases, the phase transition shifts to higher temperature and the density increases slightly, whereas fractional volume change decreases. A decrease in the value of transition entropy, order parameters and dT_{NI}/dp is found whereas the

Table 1. The DNI transition parameters under high pressure $\bar{P}_{2NI}$ and $\bar{P}_{4NI}$ are order parameters, η is the discotic-nematic packing fraction, $\Delta\eta/\eta$ the density discontinuity, $\Delta S/Nk$ the transition entropy, $\Gamma(T_{NI}) = (\partial \ln T/\partial \ln \rho)\bar{P}_{2NI}$ and (dT_{NI}/dp) is the pressure dependence of the transition temperature T_{NI}, $C_i/C_q = 8$

x	C^*_i/k	P(bar)	T_{NI}	η	$\Delta\eta/\eta$	$\bar{P}_{2NI}$	$\bar{P}_{4NI}$	$\Delta S/Nk$	dT_{NI}/dp	$\Gamma(T_{NI})$
0.7	4500	1	603.01	0.492	0.086	0.607	0.252	1.784	179.81	1.659
		100	619.91	0.494	0.066	0.582	0.230	1.505	158.37	1.668
		200	634.31	0.498	0.054	0.569	0.220	1.357	141.27	1.681
		300	648.97	0 501	0 044	0 548	0.202	1 199	129.43	1.691
		400	661.41	0.505	0.038	0.538	0.195	1.115	118 96	1.702
		500	673 16	0 508	0.034	0.529	0.188	1.044	110.46	1 713
0.8	5500	1	653 31	0.526	0.034	0 522	0.181	1.111	99 43	1.545
		100	644.53	0.530	0 029	0 517	0 178	1.052	91.49	1.551
		200	654 73	0 533	0.025	0.500	0 165	0 952	85 32	1.555
		300	663 04	0 536	0.022	0.495	0.162	0.909	79.48	1 561
		400	670.55	0.540	0.021	0 493	0 160	0.883	74 40	1.566
		500	677.83	0 543	0 019	0 489	0.158	0 855	70.09	1 571
0.9	6500	1	679.86	0.550	0.019	0 485	0.154	0.888	69 14	1.456
		100	686.56	0.553	0.018	0 481	0.152	0.856	64.78	1.458
		200	692.82	0.556	0 016	0.479	0.150	0.832	60.94	1.460
		300	698.71	0.559	0.015	0.477	0 149	0.813	57.58	1.462
		400	705 11	0.561	0.014	0.469	0.143	0.773	54.80	1.464
		500	710.34	0.564	0.013	0 468	0 142	0.761	52 12	1.466

C^*_i/k	C_i/C_q	P(bar)	T_{NI}	η	$\Delta\eta/\eta$	$\tilde{P}_{2NI}$	$\tilde{P}_{4NI}$	$\Delta S/Nk$	dT_{NI}/dp	$\Gamma(T_{NI})$
4500	8	100	738.56	0.467	0.120	0.725	0.386	2.964	300.85	1.80
		300	792.45	0.461	0.115	0.661	0.311	2.001	235.38	1.82
		500	835.79	0.465	0.080	0.622	0.271	1.586	197.56	1.85
	20	100	634.92	0.488	0.101	0.651	0.301	2.002	191.36	1.97
		300	670.35	0.492	0.066	0.608	0.259	1.528	158.89	2.00
		500	700.01	0.497	0.050	0.584	0.237	1.298	137.24	2.04
	50	300	614.00	0.509	0.050	0.586	0.239	1.351	129.73	2.13
		500	637.74	0.516	0.040	0.573	0.228	1.208	113.42	2.17
5500	8	100	896.15	0.468	0.214	0.731	0.395	3.107	311.98	1.80
		300	951.63	0.462	0.131	0.677	0.329	2.196	248.21	1.81
		500	997.84	0.463	0.094	0.640	0.289	1.756	212.17	1.83
	20	100	771.02	0.489	0.106	0.660	0.310	2.087	194.38	1.97
		300	807.37	0.491	0.074	0.622	0.272	1.652	165.45	1.99
		500	839.89	0.494	0.056	0.592	0.244	1.382	146.19	2.02
	50	100	711.94	0.504	0.074	0.623	0.274	1.721	155.23	2.08
		300	741.47	0.507	0.055	0.593	0.246	1.419	135.09	2.11
		500	765.92	0.513	0.045	0.583	0.236	1.286	119.69	2.15
6500	8	100	1053.05	0.469	0.225	0.736	0.402	3.228	319.87	1.80
		300	1110.22	0.463	0.144	0.689	0.343	2.354	258.45	1.81
		500	1159.78	0.462	0.105	0.651	0.301	1.885	224.87	1.82
	20	100	908.49	0.488	0.109	0.659	0.309	2.111	198.36	1.96
		300	948.96	0.489	0.079	0.624	0.274	1.700	172.07	1.98
		500	978.09	0.493	0.062	0.604	0.255	1.478	152.73	2.01
	50	100	838.62	0.503	0.076	0.625	0.275	1.748	157.25	2.08
		300	868.23	0.506	0.058	0.600	0.252	1.478	139.05	2.11
		500	895.10	0.510	0.048	0.584	0.237	1.313	125.36	2.14

parameter Γ increases slightly. At a given pressure with the increasing values of the interaction strength ratio the values of transition temperature, fracional volume change, transition entropy, order parameter and (dT_{NI}/dp) decreases but the values of the packing fraction and the parameter Γ increases. It is also observed that the range of stability of the discotic nematic phase is considerably larger at constant density as compared to its stability range at constant pressure.

For the ordinary nematic phase ($x > 1$) we calculate the thermodynamic properties of nematic-isotropic (NI) phase transition. We observe that the transition properties of ordinary nematic phase vary in a similar way as in case of discotic nematic phase (discussed above). We observe discontinuity in the transition properties near $x = 1.0$ (a system of hard ellipsoidal molecule) for which the anisotropic part of the potential is zero. It is observed that all the transition properties vary smoothly around $x = 1.0$, packing fraction is maximum whereas order parameter and relative change in density at the transition are minimum. We observe a remarkable symmetry in phase transition properties of discotic nematic ($x < 1$) and ordinary nematic ($x > 1$) phases which is in agreement with Monte-Carlo simulation of Frankel *et al* [22]. This is expected physically because in ordinary nematics, the role of director is played by the average orientation of the long axes of molecules while in discotic nematic the director is normal to the plane of the predominant orientation of molecules [23]. Also, discotic nematic phase having symmetry $D_{\infty h} \times T(3)$ is analogue of the ordinary nematic phase. It is distinguished from nematic phase formed by rod shape molecules only by indications of the anisotropy of the dielectric permittivity and other tensor characteristics.

References

[1] Y Singh and S Singh 1982 *Mol Cryst Liq Cryst* **87** 211
[2] P J Flory and G Ronca 1979 *Mol Cryst Liq Cryst* **54** 289
[3] M Warner 1980 *J Chem Phys* **73** 6327, 1982 *Mol Cryst Liq Cryst* **80** 79
[4] F Dowell 1983 *Phys Rev* **28A** 3520, 1985 *ibid* **31A** 2464
[5] J G Ypma and G Vertogen 1978 *Phys Rev* **A17** 1490
[6] K L Savithramma and N V Madhusudana 1980 *Mol Cryst Liq Cryst* **62** 63
[7] S Singh and K Singh 1983 *Mol. Cryst Liq Cryst* **101** 77
[8] W M Gelbert and B A Baron 1977 *J Chem Phys* **66** 207
[9] R Alben 1971 *Mol Cryst Liq Cryst* **13** 193
[10] Y Singh 1984 *Phys Rev* **A30** 583
[11] M D Lipkin and D W Oxtoby 1983 *J Chem Phys.* **79** 1939
[12] T J Slucking and P Shukla 1983 *J Phys* **A16** 1539
[13] U P Singh and Y Singh 1986 *Phys Rev* **A33** 2725
[14] J L Lebowitz and J K Percus 1963 *J Math Phys* **4** 116
[15] A J M Yang, P D Fleming III and J H Gibbs 1976 *J Chem Phys* **64** 3732
[16] W Maier and A Saupe 1959 *Z Naturforsch* **14A** 882; 1960 *ibid* **15A** 287
[17] M A Cotter 1977 *J Chem Phys* **66** 1098
[18] K Singh, U P Singh and S Singh 1988 *Liq Cryst* **3** 617 (referred in the text as I)
[19] J D Parson 1979 *Phys Rev.* **A19** 1225
[20] B J Berne and P Pechukas 1972 *J Chem Phys* **56** 4213
[21] B Larsen, J G Rasaiah and G Stell G 1977 *Mol Phys* **33** 987
[22] D Frankel, B M Mulder and J P Mc Togue 1974 *Phys Rev Lett.* **52** 287